

10/568,388

EAST Search History

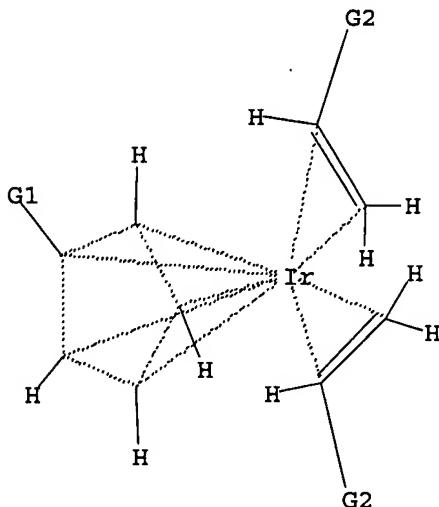
Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	998	(556/136).CCLS.	US-PGPUB; USPAT; EPO; JPO	OR	OFF	2007/04/19 17:17
L2	796	(427/252).CCLS.	US-PGPUB; USPAT; EPO; JPO	OR	OFF	2007/04/19 17:17

10/568,388

(FILE 'HOME' ENTERED AT 13:11:26 ON 19 APR 2007)

FILE 'REGISTRY' ENTERED AT 13:11:46 ON 19 APR 2007
L1 STRUCTURE uploaded

=> d l1
L1 HAS NO ANSWERS
L1 STR



G1 Me,Et,n-Pr,i-Pr,n-Bu,i-Bu,s-Bu,t-Bu
G2 Me,Et,n-Pr,i-Pr,n-Bu,i-Bu,s-Bu,t-Bu,H

Structure attributes must be viewed using STN Express query preparation.

=> s l1
SAMPLE SEARCH INITIATED 13:12:35 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 4082 TO ITERATE

49.0% PROCESSED 2000 ITERATIONS 0 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 77809 TO 85471
PROJECTED ANSWERS: 0 TO 0

L2 0 SEA SSS SAM L1

=> s l1 full
FULL SEARCH INITIATED 13:12:42 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 81747 TO ITERATE

100.0% PROCESSED 81747 ITERATIONS 2 ANSWERS
SEARCH TIME: 00.00.01

L3 2 SEA SSS FUL L1

=> fil caplus
COST IN U.S. DOLLARS SINCE FILE TOTAL
FULL ESTIMATED COST ENTRY SESSION
172.55 172.76

FILE 'CAPLUS' ENTERED AT 13:12:48 ON 19 APR 2007
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FILE COVERS 1907 - 19 Apr 2007 VOL 146 ISS 17
FILE LAST UPDATED: 18 Apr 2007 (20070418/ED)

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<http://www.cas.org/infopolicy.html>

=> s 13
L4 2 L3

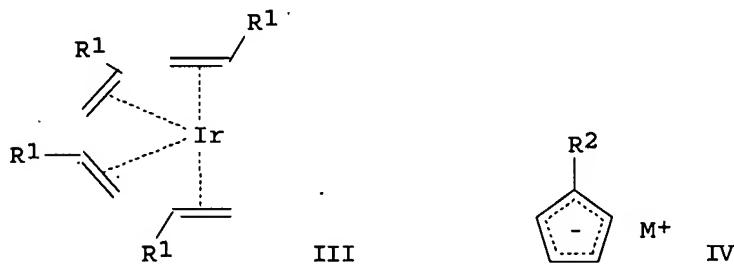
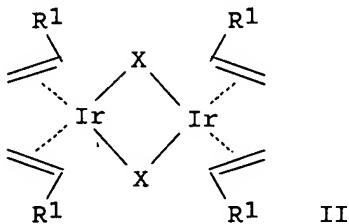
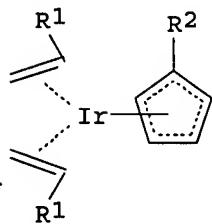
=> d 1-2 bib abs

L4 ANSWER 1 OF 2 CAPLUS COPYRIGHT 2007 ACS on STN
AN 2006:1092415 CAPLUS
DN 146:37159
TI Fabrication of Ir-based electrodes by metal organic chemical vapor deposition using liquid Ir precursors
AU Fujisawa, Hironori; Watari, Soichi; Iwamoto, Naoya; Shimizu, Masaru; Furukawa, Taishi; Kawano, Kazuhisa; Oshima, Noriaki
CS Department of Electrical Engineering and Computer Sciences, Graduate School of Engineering, University of Hyogo, 2167 Shosha, Himeji, Hyogo, 671-2201, Japan
SO Japanese Journal of Applied Physics, Part 1: Regular Papers, Brief Communications & Review Papers (2006), 45(9B), 7354-7359
CODEN: JAPNDE
PB Japan Society of Applied Physics
DT Journal
LA English
AB Ir-based electrodes were fabricated by metal organic CVD (MOCVD) using a newly developed liquid precursor, (ethylcyclopentadienyl)bis(ethylene)iridium [Ir(EtCp)(C₂H₄)₂], with a lower decomposition temperature than previous precursors, (ethylcyclopentadienyl)(1,5-cyclooctadiene) iridium [Ir(EtCp)(COD)] and (ethylcyclopentadienyl)(1,3-cyclohexadiene) iridium [Ir(EtCp)(CHD)]. Film growth behavior during MOCVD using Ir(EtCp)(C₂H₄)₂ was studied and compared with that using Ir(EtCp)(COD) and Ir(EtCp)(CHD). When Ir(EtCp)(C₂H₄)₂ was used, significantly higher nucleation was observed at the initial growth stage than that using Ir(EtCp)(COD) and Ir(EtCp)(CHD) owing to the lower thermal decomposition temperature of 220°. Ir, IrO₂ and Ir/IrO₂ films were successfully prepared using Ir(EtCp)(C₂H₄)₂ on underlying SiO₂, TiN and Pb(Zr,Ti)O₃, showing that Ir-based top and bottom electrodes can be fabricated by MOCVD. The root-mean-square surface roughnesses and elec. resistivities of Ir and IrO₂ films on SiO₂ were 2.2 nm and 9.4 μΩ cm, and 3.3 nm and 1.8 + 10² μΩ cm, resp. The step coverage of Ir films prepared at 230-400° were 35-45%.
RE.CNT 21 THERE ARE 21 CITED REFERENCES AVAILABLE FOR THIS RECORD

ALL CITATIONS AVAILABLE IN THE RE FORMAT

L4 ANSWER 2 OF 2 CAPLUS COPYRIGHT 2007 ACS on STN
 AN 2005:161097 CAPLUS
 DN 142:261654
 TI Organoiridium compound, process for producing the same, and process for
 producing film
 IN Kawano, Kazuhisa; Takamori, Mayumi; Oshima, Noriaki
 PA Tosoh Corporation, Japan; Sagami Chemical Research Center
 SO PCT Int. Appl., 17 pp.
 CODEN: PIXXD2
 DT Patent
 LA Japanese
 FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	WO 2005017950	A2	20050224	WO 2004-JP11796	20040811
	WO 2005017950	A3	20050331		
	W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW RW: BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW, AM, AZ, BY, KG, KZ, MD, RU, TJ, TM, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG				
	JP 2005225855	A	20050825	JP 2004-191388	20040629
	EP 1657245	A2	20060517	EP 2004-771757	20040811
	R: DE, FR, GB				
	CN 1835961	A	20060920	CN 2004-80023620	20040811
	US 2006204660	A1	20060914	US 2006-568388	20060215
PRAI	JP 2003-295329	A	20030819		
	JP 2003-383169	A	20031112		
	JP 2004-5503	A	20040113		
	WO 2004-JP11796	W	20040811		
OS	MARPAT 142:261654				
GI					



AB There are provided an organoiridium compound represented by the general formula (I) ($R_1 = H$, lower alkyl; $R_2 = \text{lower alkyl}$) which has a low m.p. and excellent vaporization characteristics, exhibit thermal decomposition at lower temperature compared to existing material, and can deposit a film on substrates at low temps.; and a process for producing an iridium-containing film from the organometallic compound A compound represented by the general formula (II) or the general formula (III) (wherein $R_1 = \text{same as above}$; $X = \text{halo}$) is reacted with a compound represented by the general formula (IV) ($R_2 = \text{same as above}$; $M = \text{alkali metal}$) to obtain an organoiridium compound I, e.g., (ethylcyclopentadienyl)bis(ethylene)iridium (V). This compound is used as a raw material to produce an iridium-containing film having excellent step coverage property by chemical vapor deposition process. Thus, 49 mg di(μ -chloro)tetrakis(ethylene)diiridium(I) was added to 10 mL THF, cooled to -78°, treated with a solution of 17 mg lithium ethylcyclopentadienide in 10 mL, stirred at -78° for 30 min, warmed to room temperature, allowed to react for 1 h, concentrated to a muddy mixture, and extracted with hexane to give, after alumina chromatog. of the hexane extract,

14

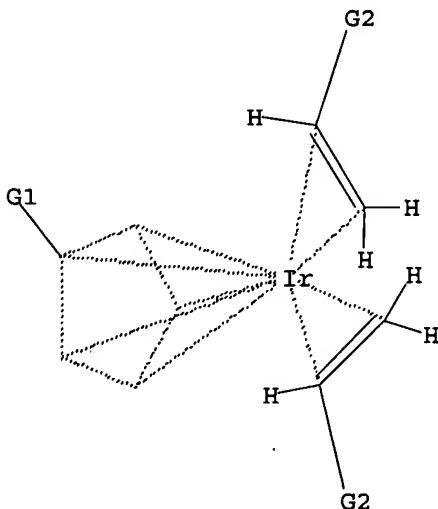
mg V. V was used to deposit 300 nm iridium film on 100 nm SiO_2 film-coated silicon substrate using N carrier gas and O as oxidizing gas at 400° substrate temperature and 10 Torr.

10/568,388

(FILE 'HOME' ENTERED AT 12:56:30 ON 19 APR 2007)

FILE 'REGISTRY' ENTERED AT 12:57:17 ON 19 APR 2007
L1 STRUCTURE uploaded

=> d l1
L1 HAS NO ANSWERS
L1 STR



G1 Me,Et,n-Pr,i-Pr,n-Bu,i-Bu,s-Bu,t-Bu
G2 Me,Et,n-Pr,i-Pr,n-Bu,i-Bu,s-Bu,t-Bu,H

Structure attributes must be viewed using STN Express query preparation.

=> s l1
SAMPLE SEARCH INITIATED 12:58:01 FILE 'REGISTRY'
SAMPLE SCREEN SEARCH COMPLETED - 4082 TO ITERATE

49.0% PROCESSED 2000 ITERATIONS 1 ANSWERS
INCOMPLETE SEARCH (SYSTEM LIMIT EXCEEDED)
SEARCH TIME: 00.00.01

FULL FILE PROJECTIONS: ONLINE **COMPLETE**
BATCH **COMPLETE**
PROJECTED ITERATIONS: 77809 TO 85471
PROJECTED ANSWERS: 1 TO 125

L2 1 SEA SSS SAM L1

=> s l1 full
FULL SEARCH INITIATED 12:58:06 FILE 'REGISTRY'
FULL SCREEN SEARCH COMPLETED - 81747 TO ITERATE

100.0% PROCESSED 81747 ITERATIONS 24 ANSWERS
SEARCH TIME: 00.00.01

L3 24 SEA SSS FUL L1

=> fil caplus
COST IN U.S. DOLLARS SINCE FILE TOTAL
FULL ESTIMATED COST ENTRY SESSION
172.55 172.76

FILE 'CAPLUS' ENTERED AT 12:58:11 ON 19 APR 2007
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FILE COVERS 1907 - 19 Apr 2007 VOL 146 ISS 17
FILE LAST UPDATED: 18 Apr 2007 (20070418/ED)

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=> s 13
L4 31 L3

=> s 14 and py<=2003
23917454 PY<=2003
L5 28 L4 AND PY<=2003

=> d 1-28 bib abs

L5 ANSWER 1 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 2003:47783 CAPLUS
DN 138:401869
TI Half-sandwich-type complexes of iridium with tetramethylcyclopentadienyl as ligand
AU Mahr, A.; Nurnberg, O.; Werner, H.
CS Inst. fuer Anorganische Chemie der Universitat, Wurzburg, Germany
SO Zeitschrift fuer Anorganische und Allgemeine Chemie (2003),
629(1), 91-98
CODEN: ZAACAB; ISSN: 0044-2313
PB Wiley-VCH Verlag GmbH & Co. KGaA
DT Journal
LA German
OS CASREACT 138:401869
AB The Ir(I) complexes $[(\eta^5\text{-C}_5\text{HMe}_4)\text{Ir}(\text{C}_2\text{H}_4)_2]$ and $[(\eta^5\text{-C}_5\text{HMe}_4)\text{Ir}(\text{CO})_2]$, which were prepared from $[\text{IrCl}(\text{C}_2\text{H}_4)_2]_2$ or $[\text{IrCl}(\text{CO})_3]_n$ and LiC_5HMe_4 , react with tosyl chloride as well as with X_2 ($\text{X} = \text{Cl}$, Br , iodo) by oxidative addition to yield the corresponding Ir(III) compds. Treating $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrX}_2]_n$ ($\text{X} = \text{Cl}$ 7, Br 8, iodo 9) with CO or PR_3 ($\text{R} = \text{Me}$, Ph) leads to cleavage of the halide bridges and to the formation of mononuclear $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrX}_2(\text{CO})]$ ($\text{X} = \text{Br}$, iodo) and $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrX}_2(\text{PR}_3)]$ ($\text{X} = \text{Cl}$, Br , iodo; $\text{R} = \text{Me}$, Ph, i-Pr, tert-Bu), resp. The mol. structure of $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrBr}_2(\text{PiPr}_3)]$ was determined crystallog., [monoclinic, space group $\text{P}21/n$, $a = 9.4150(10)$, $b = 12.896(2)$, $c = 17.181(2)$ Å, $\beta = 92.490(9)^\circ$, $Z = 4$]. The reactions of 8 and 9 with $\text{Ph}_2(\text{CH}_2)_n\text{PPh}_2$ ($n = 1$ or 2) afford the bridged compds. $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrX}_2]_2\{\mu\text{-}\text{Ph}_2(\text{CH}_2)_n\text{PPh}_2\}$ ($\text{X} = \text{Br}$, iodo; $n = 1, 2$). The dihalide complexes $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrI}_2(\text{PPh}_3)]$ and $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrX}_2(\text{PiPr}_3)]$ ($\text{X} = \text{Cl}$, Br , iodo) react with hydride sources to give the dihydrido- and monohydrido derivs. $[(\eta^5\text{-C}_5\text{HMe}_4)\text{IrH}_2(\text{PPh}_3)]$

and $[(\eta_5\text{-C}_5\text{HMe}_4)\text{IrH}(\text{X})(\text{PiPr}_3)]$ ($\text{X} = \text{Cl}, \text{Br}, \text{iodo}$). The related di-Me and monomethyl compds. $[(\eta_5\text{-C}_5\text{HMe}_4)\text{IrMe}_2(\text{PiPr}_3)]$ and $[(\eta_5\text{-C}_5\text{HMe}_4)\text{IrCH}_3(\text{I})(\text{PiPr}_3)]$ were obtained from the dihalide precursors $[(\eta_5\text{-C}_5\text{HMe}_4)\text{IrX}_2(\text{PiPr}_3)]$ ($\text{X} = \text{Br}, \text{iodo}$) and CH_3MgI in the molar ratio of 1:2 or 1:1, resp.

RE.CNT 27 THERE ARE 27 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 2 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 2002:881497 CAPLUS
DN 139:261337
TI Product class 8: four-membered rings with one or more heteroatoms
AU Regitz, M.; Bergstraesser, U.
CS Germany
SO Science of Synthesis (2002), 9, 135-181
CODEN: SSCYJ9
PB Georg Thieme Verlag
DT Journal; General Review
LA English
AB A review describes the synthesis of various compds. containing four-membered rings with one or more heteroatoms. Covered reactions include ring transformations and ring-closure reactions.

RE.CNT 288 THERE ARE 288 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 3 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 2002:881458 CAPLUS
DN 139:350763
TI Product class 6: organometallic complexes of iridium
AU O'Connor, J. M.
CS Dept. of Chemistry & Biochemistry, University of California - San Diego, La Jolla, CA, 92093-0358, USA
SO Science of Synthesis (2002), 1, 617-744
CODEN: SSCYJ9
PB Georg Thieme Verlag
DT Journal; General Review
LA English
AB A review on the preparation and applications of iridium organometallic complexes.

RE.CNT 373 THERE ARE 373 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 4 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 2002:444615 CAPLUS
DN 137:279281
TI Formation of planar-chiral alkylphosphine- and aniline-substituted cyclopentadienyl metal complexes and their reactivity toward electrophiles
AU Paisner, Sara N.; Lavoie, Gino G.; Bergman, Robert G.
CS Department of Chemistry and the Center for New Directions in Organic Synthesis (CNDOS), University of California, Berkeley, CA, 94720-1460, USA
SO Inorganica Chimica Acta (2002), 334, 253-275
CODEN: ICHAA3; ISSN: 0020-1693
PB Elsevier Science B.V.
DT Journal
LA English
OS CASREACT 137:279281
AB A wide range of transition metal complexes containing aniline- and alkylphosphine-substituted cyclopentadienyl ligands have been synthesized: $\text{CpP}\text{Ir}(\text{CH}_3)_2$ (5), $\text{CpP}\text{Ir}(\text{H})(\text{Li})$ (11a,b), $\text{CpP}\text{Ir}(\text{H})(\text{SnPh}_3)$ (13a,b) ($\text{CpP} = 1\text{-}(2\text{-dimethylphosphino-1,1-dimethylethyl})\text{-}3\text{-tert-butylcyclopentadienyl}$), $\text{CpN}\text{Ir}(\text{C}_2\text{H}_4)_2$ (7), CpNIrI_2 (8), $\text{CpN}\text{Ir}(\text{O}_3\text{SCF}_3)_2$ (9), $\text{CpN}(\text{PM}_3)\text{IrI}_2$ (10), $\text{CpN}(\text{PM}_3)\text{IrH}_2$ (2), $\text{CpN}(\text{PM}_3)\text{Ir}(\text{H})(\text{Li})$ (15a,b), $\text{CpN}(\text{PM}_3)\text{Ir}(\text{H})(\text{SnPh}_3)$ (16a,b) ($\text{CpN} = 1\text{-}(2\text{-dimethylamino)phenyl-3-tert-butylcyclopentadienyl}$), CpPZrCl_3 (18), $\text{CpPZr}(\text{CH}_2\text{Ph})_3$ (23), $\text{CpPZr}(\text{CH}_2\text{Ph})_2\text{Cl}$ (20), $[(\text{CpP})\text{TiCl}_3]_2$

(22), CpNCp'ZrCl₂ (Cp' = Cp (23), Cp* (24)), and CpPCp'ZrCl₂ (Cp' = Cp (25), Cp* (26)). The presence of the planar-chiral CpP and CpN ligands dramatically changes the reactivity at the metal center in comparison to that of the analogous unchelated and achiral pentamethylcyclopentadienyl (Cp*) complexes. Lithium salts 11 and 15 were obtained by deprotonation of dihydride 2 and the earlier prepared dihydride CpPIrH₂ (1) with tert-butyllithium; these reactive species show diastereoselectivity in their reactions with Ph₃SnCl to form 13a,b and 16a,b, resp. One enantiomer of diiodide 3 was found to react selectively with (R)-binaphthol to form (R,R)-CpPIr(binaphtholate) (17a) leaving (S)-3 unreacted. Attempts to sep. the enantiomers of 3 and 17a were unsuccessful, however, due to the lack of difference in their solubility DFT calcns. carried out on the two possible diastereomers 17a and 17b correctly predict the exclusive formation of 17a. The zirconium and titanium complexes catalyze the polymerization of ethylene to polyethylene and propylene to isotactic polypropylene in the presence of MAO co-catalyst. Compds. 24 and 26 can be methylated to form Cp'Cp'ZrMe₂ (Cp' = CpN (27), CpP (28)).

RE.CNT 58 THERE ARE 58 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5	ANSWER 5 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN			
AN	2001:661433 CAPLUS			
DN	135:211151			
TI	Selective and thermally induced borylation of primary C-H bonds in hydrocarbons catalyzed by iridium and rhodium organometallic complexes			
IN	Chen, Huiyan; Hartwig, John F.; Semple, Thomas Carl			
PA	Shell Internationale Research Maatschappij BV, Yale University			
SO	PCT Int. Appl., 66 pp.			
	CODEN: PIXXD2			
DT	Patent			
LA	English			
FAN.CNT 1				
	PATENT NO.	KIND	DATE	APPLICATION NO.
	-----	-----	-----	-----
PI	WO 2001064689	A1	20010907	WO 2001-EP2407
	W: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, UZ, VN, YU, ZA, ZW			20010301 <--
	RW: GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW, AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR, BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG			
	US 6451937	B1	20020917	US 2000-516897
	CA 2401695	A1	20010907	CA 2001-2401695
	EP 1259517	A1	20021127	EP 2001-909815
	EP 1259517	B1	20030917	
	R: AT, BE, CH, DE, DK, ES, FR, GB, GR, IT, LI, LU, NL, SE, MC, PT, IE, SI, LT, LV, FI, RO, MK, CY, AL, TR			
	JP 2003525300	T	20030826	JP 2001-564185
	AT 250069	T	20031015	AT 2001-909815
	CN 1524084	A	20040825	CN 2001-807302
	ZA 2002007214	A	20030717	ZA 2002-7214
	AU 2004201832	A1	20040520	AU 2004-201832
PRAI	US 2000-516897	A	20000301	
	WO 2001-EP2407	W	20010301	
OS	CASREACT 135:211151			
AB	A process for selectively functionalizing an aliphatic hydrocarbon and/or alkyl branched alicyclic hydrocarbon at a primary C-H hydrocarbon bond comprising thermally reacting a functionalizing reagent and the hydrocarbon in the presence of a catalyst, said catalyst comprising: (a) a source of a transition metal; (b) a source of a 3 to 8, cyclic or			

noncyclic, aromatic or nonarom., neutral, cationic or anionic, substituted or unsubstituted, electron donor moiety which does not dissociate under thermal reaction conditions, wherein said moiety (i) lacks aromatic C-H bonds on the moiety directly bonded to the transition metal, or (ii) contains sterically hindered aromatic C-H bonds on the moiety directly bonded to the transition metal; and (c) a source of ligands capable of formally donating an electron pair to the transition metal of (a) and which dissociate thermally; and wherein said functionalizing reagent comprises a source of boron. For example, in a dry box, a solution containing 0.00125 mmol of the Cp*^{*}Rh(C₂H₂)₂ catalyst and 31.7 mg (0.125 mmol) B₂pin₂ (B₂pin₂ = (OCMe₂CMe₂O)BB(OCMe₂CMe₂O)) in 0.7 mL of dry n-octane was placed in a screw-cap NMR sample tube and sealed tightly. The sample was removed from the box and placed in a 150 °C oil bath. The solution was heated for 80 h at 150 °C and monitored periodically by ¹¹B NMR spectroscopy until HBpin was completely consumed. The sample was brought into the dry box and a solution of dodecahydrotriphenylene (15.2 mg, 0.0632 mmol; reference) in

benzene was added by pipet. An aliquot was then removed and analyzed by GC. The yield of the (1-octyl)Bpin functionalized product was 72%; 100% of the B₂pin₂ was reacted. The catalyst turnover count was 144. The amount of time taken to convert B₂pin₂ was 80 min. The selectivity toward the 1-octylBpin product at the primary C-H bond was exclusive, 99.9+. Other octyl byproducts were not detected. Other catalysts described in examples include: Cp*Ir(C₂H₂)₂, Cp*^{*}Rh(CH₂:CHSiMe₃)₂, Cp*^{*}RhH₂(SiEt₃)₂ and [(η₄-C₆Me₆)Rh(η₅-C₅Me₅)].

RE.CNT 5 THERE ARE 5 CITED REFERENCES AVAILABLE FOR THIS RECORD
ALL CITATIONS AVAILABLE IN THE RE FORMAT

L5 ANSWER 6 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1996:156881 CAPLUS
DN 124:261325
TI "Solvent-Free" Photochemical Activation of CH₄, C₂H₄, and C₂H₆ by (C₅Me₅)Ir(CO)₂ in Supercritical Fluid Solution
AU Banister, James A.; Cooper, Andrew I.; Howdle, Steven M.; Jobling, Margaret; Poliakoff, Martyn
CS Department of Chemistry, University of Nottingham, Nottingham, NG7 2RD, UK
SO Organometallics (1996), 15(7), 1804-12
CODEN: ORGND7; ISSN: 0276-7333
PB American Chemical Society
DT Journal
LA English
AB The activation of H₂ and light hydrocarbons (CH₄, C₂H₄, and C₂H₆) by Cp*Ir(CO)₂ (Cp* = η₅-C₅Me₅) in supercrit. fluid solution is described. The reactions have been carried out both in the presence of a supercrit. solvent (scCO₂, scXe, or scCHF₃) or "solvent-free" in the pure supercrit. hydrocarbon (scCH₄, scC₂H₄, or scC₂H₆). This is the first use of scCH₄ as a solvent for photochem. reactions. The presence of H₂ in scC₂H₆ greatly enhances the effectiveness of the C-H activation, but even in the presence of D₂, Cp*Ir(CO)(H)Et and not Cp*Ir(CO)(D)Et is formed. Reaction of Cp*Ir(CO)₂ with H₂ occurs efficiently in CHF₃, but C-H activation of C₂H₆ is almost suppressed in this mixed scC₂H₆/scCHF₃ fluid, possibly through H-bonding to the metal center. A technique for recovering the products from milligram-scale reactions is described.

L5 ANSWER 7 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1995:793495 CAPLUS
DN 124:8966
TI Aryldiazenido complexes: structure, fluxionality, and properties of the iridium ethylene aryldiazenido complex [(η₅-C₅Me₅)Ir(C₂H₄)(p-N₂C₆H₄OMe)][BF₄] and a comparison with the analogous nitrosyl complex [(η₅-C₅Me₅)Ir(C₂H₄)(NO)][BF₄]
AU Yan, Xiaoqian; Einstein, Frederick W. B.; Sutton, Derek
CS Dep. Chem., Simon Fraser Univ., Burnaby, BC, V5A 1S6, Can.
SO Canadian Journal of Chemistry (1995), 73(7), 939-55

PB CODEN: CJCHAG; ISSN: 0008-4042
DT National Research Council of Canada
LA Journal
OS English
OS CASREACT 124:8966

AB [Cp*Ir(C₂H₄)(N₂Ar)][BF₄] (1BF₄; Ar = C₆H₄OMe-p) was synthesized by reacting [ArN₂][BF₄] with Cp*Ir(C₂H₄)₂ at low temperature. An initial electrophilic attack of the incoming diazonium ion at Ir, followed by expulsion of C₂H₄, is postulated to account for the mild reaction conditions that are in sharp contrast to the usual inertness of the bis(ethylene) compound toward ligand substitution. The IR and N NMR data for 1BF₄ and its 15N_α derivative unambiguously establish that the ArN₂ ligand has the singly bent geometry in this complex in solution. The x-ray crystal structure confirms this for the solid state, and establishes that the plane of the aryldiazenido ligand is approx. perpendicular to the plane defined by the Ir atom and the centers of mass of the Cp* and ethylene ligands. An EHMO anal. of the singly bent aryldiazenido ligand was carried out and satisfactorily accounts for the observed orientation of the ArN₂ ligand. An anal. of the variable-temperature ¹H and ¹³C NMR of 1BF₄ indicates that both restricted rotation of the C₂H₄ ligand and a conformational isomerization of the aryldiazenido ligand are occurring, and ΔG.thermod.270 for the ethylene rotation barrier is estimated at ≤51.5 ± 0.4 kJ mol⁻¹. This is lower than the barrier of ΔG.thermod.353 = 68.7 ± 0.2 kJ mol⁻¹ determined previously for the analogous nitrosyl complex [Cp*Ir(C₂H₄)(NO)][BF₄] (2BF₄) and probably in these half-sandwich complexes both NO and ArN₂ function as single-faced π-acceptors, and in these circumstances ArN₂ is the better π-acceptor. The ethylene in 1BF₄ is readily displaced by PPh₃ to give [Cp*Ir(PPh₃)(N₂Ar)][BF₄] (3BF₄). This reacts with NaBH₄ to yield Cp*IrH(PPh₃)(N₂Ar) (4) in which the ArN₂ ligand has switched to the doubly bent geometry, on the basis of the 15N_α NMR chemical shift data. Attempts to synthesize the corresponding chloro analog 5 resulted in only the chloride salt of the singly bent ArN₂ cation 3. For example, reaction of 3BF₄ with HCl yields the aryldiazene complex [Cp*IrCl(PPh₃)(NHNAr)][BF₄] (6), but deprotonation of this with Et₃N yields 3Cl, not 5. 1BF₄ crystallized in the space group P21/n with a 8.5780(10), b 20.5310(23), c 12.0310(15) Å, β 93.500(10)°, and Z = 4. The structure was refined to R_f = 0.0281 from 2611 observed reflections with I₀ ≥ 2.5σ(I₀) in the range 2θ = 0-50° (Mo-Kα).

L5 ANSWER 8 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1995:314876 CAPLUS
DN 122:160902

TI π-Olefin iridium complexes. XXII. C-H activation of aromatic and aliphatic solvent molecules RH in the reaction of [Cp*IrCl₂]₂ with butadienemagnesium with formation of [Cp*Ir(η₃-C₄H₇)R], and crystal structure of [Cp*Ir(η₃-C₄H₇)C₆H₅]

AU Mueller, Joern; Gaede, Petra Escarpa; Qiao, Ke
CS Institut fuer Anorganische und Analytische Chemie, Technischen Universitaet Berlin, Berlin, D-10623, Germany
SO Zeitschrift fuer Naturforschung, B: Chemical Sciences (1994), 49(12), 1645-53
CODEN: ZNBSEN; ISSN: 0932-0776
PB Verlag der Zeitschrift fuer Naturforschung
DT Journal
LA German
OS CASREACT 122:160902

AB Reactions of [Cp*IrCl₂]₂ (Cp* = η₅-C₅Me₅) with [MgC₄H₆.2 THF]_n at low temperature gave [Cp*Ir(η₄-C₄H₆)] together with [Cp*Ir(η₃-C₄H₇)R] compds., the latter being formed via C-H activation of solvent mols. RH (RH = benzene, toluene, anisole, thiophene, furan, N-methylpyrrole, pentane, cyclohexane, THF). In the case of pyrrole, C-N-activation occurs. The ratio of syn and anti isomers of the 1-methylallyl complexes

as well as the sites of C-H activation of RH were investigated by NMR spectrometry. An enantiomorphous crystal of $[\text{Cp}^*\text{Ir}(\eta^3\text{-C}_4\text{H}_5)\text{C}_6\text{H}_5]$ was characterized by x-ray diffraction anal. which reveals trigonal planar coordination at the Ir atom and an exo, syn conformation of the 1-methylallyl ligand. A mechanism of the reaction which involves 16-electron intermediates is discussed. The corresponding system $[\text{Cp}^*\text{RhCl}_2]_2/\text{butadienemagnesium/RH}$ gives only $[\text{Cp}^*\text{Rh}(\eta^4\text{-C}_4\text{H}_6)]$, and no C-H activation is observed

L5 ANSWER 9 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1995:142453 CAPLUS
DN 122:81595
TI Hydrocarbon bridged complexes. XXIX. Nucleophilic addition of carbonylmetallates to cationic allyl- and alkene-complexes of tungsten, manganese, rhenium, iron, ruthenium, osmium, cobalt and iridium: σ,π -allyl and σ,σ -alkene bridged di-, tri-, and tetranuclear complexes
AU Hueffner, Stephan; Wieser, Michael; Polborn, Kurt; Beck, Wolfgang
CS Institut fuer Anorganische Chemie der Ludwig-Maximilians-Universitaet Muenchen, Meiserstrasse 1, Munchen, 80333, Germany
SO Journal of Organometallic Chemistry (1994), 481(1), 45-55
CODEN: JORCAI; ISSN: 0022-328X
PB Elsevier
DT Journal
LA German
OS CASREACT 122:81595
AB The addition of carbonylmetallates $[\text{Lm}(\text{OC})\text{nM}]^-$ to various cationic transition metal complexes with open and cyclic allyl ligands gives heterodi-, tri- and tetrametallic $\mu\text{-}\eta^1\text{:}\eta^2$ -hydrocarbon-bridged complexes in a directed way. The nucleophilic attack always takes place on a terminal carbon atom of the allyl group. The same regioselectivity was observed with $[\text{Cp}^*\text{Ir}(\eta^2\text{-C}_2\text{H}_4)(\eta^3\text{-C}_3\text{H}_5)]^+$ and $[(\text{OC})_3\text{Fe}(\eta^2\text{:}\eta^3\text{-1,2,3-bicyclooctadienyl})]^+$. The structure of $\text{Cp}^*\text{Ir}(\eta^2\text{-C}_2\text{H}_4)(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}_3\text{H}_5)\text{Re}(\text{CO})_5$ was determined by x-ray diffraction. Only with $[(\eta^6\text{-C}_6\text{H}_6)\text{Ru}(\eta^2\text{:}\eta^3\text{-C}_8\text{H}_11)]^+$ the attack of $[\text{Re}(\text{CO})_5]^-$ occurs on the alkene function of the cyclooctadienyl ligand.

L5 ANSWER 10 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1994:605639 CAPLUS
DN 121:205639
TI Rhodium and Iridium Complexes with the 1-(2-(Dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl Ligand
AU Jutzi, Peter; Kristen, Marc O.; Neumann, Beate; Stammller, Hans-Georg
CS Fakultaet fuer Chemie, Universitaet Bielefeld, Bielefeld, D-33615, Germany
SO Organometallics (1994), 13(10), 3854-61
CODEN: ORGND7; ISSN: 0276-7333
DT Journal
LA English
OS CASREACT 121:205639
AB Some new Rh(I), Rh(III), Ir(I), and Ir(III) complexes containing the 1-(2-(dimethylamino)ethyl)-2,3,4,5-tetramethylcyclopentadienyl (Cp^1) ligand are described. The bis(ethene) complexes $\text{Cp}^1\text{Rh}(\text{C}_2\text{H}_4)_2$ (2), and $\text{Cp}^1\text{Ir}(\text{C}_2\text{H}_4)_2$ (3) with a noncoordinating dimethylamino function are synthesized by reaction of $[(\text{C}_2\text{H}_4)_2\text{RhCl}]_2$ with Cp^1Li and by the reaction of $[(\text{COE})\text{IrCl}]_2$ with $\text{Cp}^1\text{Li}/\text{C}_2\text{H}_4$, resp. Addition of iodine to 2 or 3 results in the formation of the resp. diiodo complexes Cp^1RhI_2 (4) and Cp^1IrI_2 (5) with intramol. amino coordination. In the presence of CO, 4 or 5 can easily be transferred into the carbonyl complexes $\text{Cp}^1\text{RhI}_2(\text{CO})$ (6) and $\text{Cp}^1\text{IrI}_2(\text{CO})$ (7), resp., with a noncoordinating amino function. The reverse reaction is successful for both 6 and 7, but under differing conditions. In the reaction of 4 and 5 with PMe_3 , PPh_3 , and CNCMe_3 , the corresponding substitution products $\text{Cp}^1\text{MI}_2\text{L}$ (8-12) are formed. Reduction of 4 and 5 with Na-Hg under a CO atmospheric leads to the carbonyl complexes $\text{Cp}^1\text{Rh}(\text{CO})_2$ (13) and $\text{Cp}^1\text{Ir}(\text{CO})_2$ (14), resp., with a noncoordinating amino

group. In the reaction of 4 and 5 with Ag₂C₂O₄, the oxalato complexes Cp₁RhC₂O₄ (15) and Cp₁Ir(C₂O₄) (16), resp., are formed. The coordinating amino group in 15 and 16 can be replaced by the PMe₃ ligands to give Cp₁(Me₃P)Rh(C₂O₄) (17) and Cp₁Ir(PMe₃)(C₂O₄) (18). The crystal structures of 4 and 5 were determined

L5 ANSWER 11 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1994:604749 CAPLUS
DN 121:204749
TI Design and Study of Rh(III) Catalysts for the Selective Tail-to-Tail Dimerization of Methyl Acrylate
AU Hauptman, Elisabeth; Sabo-Etienne, Sylviane; White, Peter S.; Brookhart, Maurice; Garner, J. Michael; Fagan, Paul J.; Calabrese, Joseph C.
CS Department of Chemistry, University of North Carolina, Chapel Hill, NC, 27599-3290, USA
SO Journal of the American Chemical Society (1994), 116(18), 8038-60
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA English
OS CASREACT 121:204749
AB The development of an efficient, highly selective Rh(III) catalyst system for the tail-to-tail dimerization of Me acrylate (MA) to di-Me hexenedioates, precursors to adipic acid, is described. The catalytic cycle is entered by protonation of Cp*Rh(C₂H₄)₂ (Cp* = C₅Me₅) to yield Cp*Rh(C₂H₄) (CH₂CH₂-μ-H)⁺ (7) followed by reaction with Me acrylate. The catalyst resting state has been generated by low-temperature protonation of Cp*Rh(CH₂CHCO₂CH₃)₂ (15) and identified as Cp*Rh(CH₂CH₂COOMe) (η₂-CH₂CHCO₂Me)⁺ (8) by ¹H and ¹³C NMR spectroscopy. Investigation of iridium analogs has led to the isolation and X-ray structural characterization of Cp*Ir(CH₂CH₂COOMe) (η₂-CH₂CHCO₂Me)⁺ (23a), in which the orientation of the acrylate ligands is that required for tail-to-tail coupling. At -23°, complex 8 undergoes β-migratory insertion to give Cp*RhCH(CH₂COOMe) (CH₂CH₂COOMe)⁺ (10). Complex 10 was independently synthesized by treatment of complex 7 with trans-MeO₂CCH:CHCH₂CH₂CO₂Me and was characterized by X-ray crystallog. The free energy of activation for the migration reaction is 18.7 kcal/mol and matches that based on the catalytic turnover (TO) frequency (6.6 TO/min at 25 °C, ΔG.thermod. = 19 kcal/mol). This observation confirms 8 as the resting state and the C-C coupling reaction as the turnover-limiting step. The catalyst deactivates by formal loss of H₂ from complex 10 to produce Cp*Rh(η₃-CH₃OOCCH₂CHCH₂CO₂CH₃)⁺ (9). The structure of complex 9 was verified by an X-ray crystallog. study. Exposure of 9 to an atmospheric of H₂ in the presence of MA regenerates the resting state 8, and dimerization proceeds. Second generation catalysts with increased activity and lifetimes have been developed by replacing the C₅Me₅ ligand by methylated indenyl ligands. Using the catalytic system derived from (1,2,3-trimethylindenyl)Rh(C₂H₄)₂ (11), conversion of 54,000 equiv of Me acrylate to di-Me hexenedioates could be achieved after 68 h at 55 °C under N₂. Details of the mechanism have been elucidated and resemble closely those of the Cp* system. Similar intermediates to 8 and 10 have been characterized by ¹H and ¹³C NMR spectroscopy. In contrast, treatment with Me acrylate of the more electrophilic systems derived from CpRh(C₂H₄)₂ (25) (Cp = C₅H₅) and Cp.thermod.Rh(C₂H₄)₂ (30) [Cp.thermod. = C₅(CH₃)₄CF₃] results in slow dimerization. Low-temperature protonation of CpRh(CH₂CHCO₂CH₃)₂ (27) with H(Et₂O)₂BAr'₄ yields a mixture of rhodium species which upon warming to 23°C converge to the bis-chelate complex CpRhCH(CH₂COOMe) (CH₂CH₂COOMe)⁺ (28). Exposure of complex 28 to MA generates the unusual bridged species CpRh(CH₂CHCOOCH₃)H(CH₂CHCOOCH₃)⁺ (29), which serves as the resting state during dimerization. Treatment of complex 30 with H(Et₂O)₂BAr'₄ yields Cp.thermod.Rh(C₂H₄) (CH₂CH₂-μ-H)⁺ (31), which upon reaction with MA clearly produces Cp.thermod.RhCH(CH₂COOMe) (CH₂CH₂COOMe)⁺ (33), and dimerization proceeds.

Finally, attempts to catalyze the dimerization of other functionalized olefins including Me vinyl ketone, Me crotonate, 2-vinylpyridine, and 1-vinyl-2-pyrrolidinone are presented.

L5 ANSWER 12 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1994:435824 CAPLUS
DN 121:35824
TI (η 5-C5Me5)Ir(NO)(C2H4)[BF4]: Synthesis, Characterization, and Some Reactions. X-ray Crystal Structures of the Title Compound and Its Derivatives (η 5-C5Me5)Ir(NO)(CH2CH2OEt) and (η 5-C5Me5)2Ir2X2(μ -X)(μ -NO) (X = Br, I)
AU Batchelor, Raymond J.; Einstein, Frederick W. B.; Lowe, Nigel D.; Palm, Bradley A.; Yan, Xiaoqian; Sutton, Derek
CS Department of Chemistry, Simon Fraser University, Burnaby, BC, V5A 1S6, Can.
SO Organometallics (1994), 13(5), 2041-52
CODEN: ORGND7; ISSN: 0276-7333
DT Journal
LA English
OS CASREACT 121:35824
AB [$(\eta$ 5-C5Me5)Ir(NO)(C2H4)] [BF4] (1) was prepared by the reaction of (η 5-C5Me5)Ir(C2H4)2 with [NO][BF4] in acetone at -10°. The crystal structure of 1 was determined. The Ir-NO group is linear, with N-O = 1.15(1) Å, Ir-N = 1.762(9) Å, and Ir-N-O = 175.8(9)°; the IR spectrum in ethanol exhibits ν (NO) = 1821 cm⁻¹, confirmed by 15N enrichment [ν (15NO) = 1786 cm⁻¹]. The ethylene ligand is sym. bound to iridium with bond lengths Ir-C(1) = 2.19(1) Å, Ir-C(2) = 2.17(1) Å, and C(1)-C(2) = 1.37(2) Å and is oriented with the C(1)-C(2) axis approx. perpendicular to the plane defined by N and the centers of mass of the η 5-C5Me5 and η 2-C2H4 ligands, resp. The barrier to ethylene rotation was determined from variable-temperature 1H NMR data at the coalescence temperature (Tc = 353 K). Products of reaction of 1 with KI, KBr, KCl, NaOEt, and (η 5-C5Me5)Ir(CO)2 are described. Reaction with KI in ethanol at room temperature gives (η 5-C5Me5)Ir(NO)I and at 60° gives the binuclear compound (η 5-C5Me5)2Ir2I2(μ -I)(μ -NO) (2). (η 5-C5Me5)Ir(NO)I has ν (NO) = 1761 cm⁻¹ [ν (15NO) = 1717 cm⁻¹] in CDCl₃ indicating a terminal linear nitrosyl group. The crystal structure of 2-toluene was determined. Complex 2 has mutually trans η 5-C5Me5 groups, trans terminal iodide ligands, and sym. bridging nitrosyl and iodide with Ir(1)-N = 2.029(12) Å, Ir(2)-N = 1.974(12) Å, and N-O = 1.24(2) Å. The reaction of 1 with KBr in ethanol at room temperature produces (η 5-C5Me5)Ir(NO)Br in solution but this converts on attempted isolation to other products which include (η 5-C5Me5)Ir2Br2(μ -Br)(μ -NO) (3). The structure of 3 is essentially similar to that of 2, but is disordered about a crystallog. inversion center. In contrast to these ethylene displacement reactions, NaOEt reacts with 1 to produce the ethoxyethyl derivative (η 5-C5Me5)Ir(NO)(CH2CH2OEt) (4), the crystal structure of which was also determined. The reaction of 1 with (η 5-C5Me5)Ir(CO)2 in refluxing ethanol yielded [$(\eta$ 5-C5Me5)2Ir2(μ -CO)(μ -NO)][BF4], identified on the basis of anal. and spectroscopic data.

L5 ANSWER 13 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1994:322409 CAPLUS
DN 120:322409
TI Rh(III) catalysts for tail-to-tail dimerization of methyl acrylate
AU Brookhart, Maurice; Hauptman, Elisabeth; Sabo-Etienne, Sylviane
CS Dep. Chem., Univ. North Carolina Chapel Hill, North Carolina, 27599-3290, USA
SO Org. Synth. Organomet. (OSM4), Proc. Symp., 4th (1993), Meeting Date 1992, 69-77. Editor(s): Enders, Dieter; Gais, Hans-Joachim; Keim, Wilhelm. Publisher: Vieweg, Wiesbaden, Germany.
CODEN: 59SKAA

DT Conference
LA English
AB A conference in which Cp* is Me₅C₅. The development of an efficient, highly selective Rh(III) catalyst system for the tail-to-tail dimerization of Me acrylate is described. The catalytic cycle is entered by protonation of Cp*Rh(C₂H₄)₂ to yield Cp*(C₂H₄)RhCH₂CH₂-μ-H⁺, followed by reaction with Me acrylate. The catalyst resting state has been generated by low-temperature protonation of Cp*Rh(CH₂CHCO₂Me)₂ and identified. The turnover-limiting step is the C-C coupling reaction from the resting state. Addnl. low temperature NMR expts. provide a complete picture of the catalytic cycle. Investigation of Ir analogs has led to the isolation and X-ray structural characterization of a complex thought to be isostructural with the Rh resting state.

L5 ANSWER 14 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1993:259466 CAPLUS
DN 118:259466
TI Low-temperature chemical vapor deposition or laser photodeposition of metals on substrates by using organometallic compounds
IN Hicks, Robert F.; Kaesz, Herbert D.; Xu, Dagiang
PA University of California, Berkeley, USA
SO U.S., 8 pp. Cont.-in-part of U.S. Ser. No. 260,799, abandoned.
CODEN: USXXAM

DT Patent

LA English

FAN.CNT 1

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 5130172	A	19920714	US 1989-428245	19891026 <--
PRAI	US 1988-260799	B2	19881021		

AB Metals are deposited on Si or W substrates at .apprx.20-≤190° by using organometallic compound LnMRm in presence of H. L in the compound is H, ethylene, allyl, methylallyl, butadienyl, pentadienyl, cyclopentadienyl, methylcyclopentadienyl, cyclohexadienyl, hexadienyl, cycloheptatrienyl, or a derivative of these compds. having ≥1 C₅ alkyl side chain; M is a metal that can readily cycle between 2 oxidation states and can catalyze hydrogenation of hydrocarbon ligands of the compound; R is Me, Et, Pr, or Bu; and n and m are each a number from 0 to the valence of the metal. The compound is vaporized at .apprx.20-100°. M is selected from the group of metals having atomic number 22-29, 40-47, and 72-79 or 25-29, 42-47, and 74-79 or Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, and W.

L5 ANSWER 15 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1993:213268 CAPLUS

DN 118:213268

TI Synthesis and isolation of highly reactive η₃-allyl alkyne complexes of iridium via the inner-sphere η₃-allyl triflate complex (C₅Me₅)Ir(η₃-C₃H₅)OTf. Facile conversion to alkyne metallacyclobutane complexes by nucleophilic addition

AU Schwiebert, Kathryn E.; Stryker, Jeffrey M.

CS Dep. Chem., Univ. Alberta, Edmonton, AB, T6G 2G2, Can.

SO Organometallics (1993), 12(3), 600-2

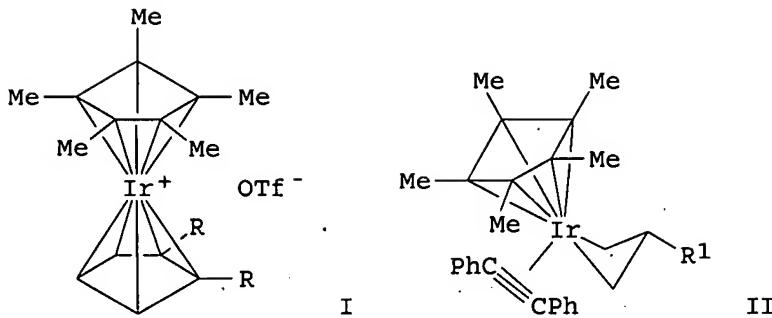
CODEN: ORGND7; ISSN: 0276-7333

DT Journal

LA English

OS CASREACT 118:213268

GI



AB The inner-sphere triflate complex $[(C_5Me_5)Ir(\eta^3\text{-}C_3H_5)OTf]$, formed quant. on photolysis of $[(C_5Me_5)Ir(\eta^3\text{-}C_3H_5)(\eta^2\text{-}C_3H_6)] + OTf^-$, reacts with disubstituted alkynes to form the isolable, but highly reactive, allyl alkyne complexes $[(C_5Me_5)Ir(\eta^3\text{-}C_3H_5)(RC\text{.tptbond.}CR)] + OTf^-$ ($R = Me, Ph$), inaccessible by conventional methodol. Although the allyl alkyne complexes undergo facile reductive ligand coupling to form the substituted bis(cyclopentadienyl) complexes I, these complexes can be isolated and converted selectively to the metallacyclobutane alkyne complexes II ($R_1 = H, Me, CN, MeCHBz$) in high yield by reaction with nucleophiles.

L5 ANSWER 16 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1992:408168 CAPLUS

DN 117:8168

TI Mechanism of rhodium(III)-catalyzed methyl acrylate dimerization

AU Brookhart, Maurice; Hauptman, Elisabeth

CS Dep. Chem., Univ. North Carolina, Chapel Hill, NC, 27599-3290, USA

SO Journal of the American Chemical Society (1992), 114(11), 4437-9

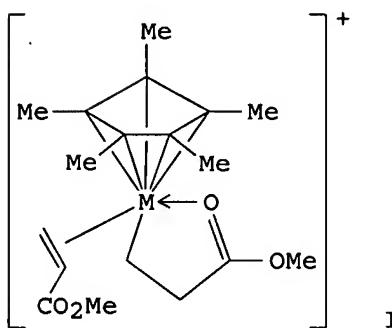
CODEN: JACSAT; ISSN: 0002-7863

DT Journal

LA English

OS CASREACT 117:8168

GI



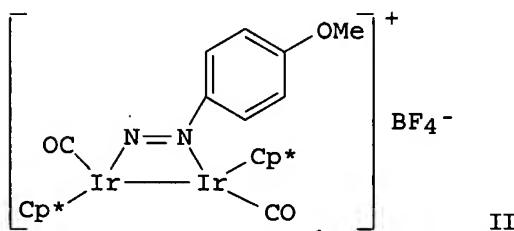
AB Protonation of $Cp^*\text{Rh}(C_2H_4)_2$ ($Cp^* = \eta^5\text{-pentamethylcyclopentadienyl}$) in the presence of Me acrylate generates a highly efficient catalytic system for the selective tail-to-tail dimerization of Me acrylate. Mechanistic details of this cycle have been elucidated. The catalyst resting state was generated by protonation of $Cp^*\text{Rh}(CH_2:\text{CHCO}_2\text{Me})_2$ at -78° and identified by ^1H and ^{13}C NMR spectroscopy as complex I ($M = \text{Rh}$). The analogous I ($M = \text{Ir}$) was synthesized; x-ray anal. of which strongly suggests, by comparison, a structure of I ($M = \text{Rh}$) in which the orientation of the acrylate ligands is that required for tail-to-tail coupling. At -23° I ($M = \text{Rh}$) undergoes β -migratory insertion to give $Cp^*\text{RhCH}(\text{CH}_2\text{CO}_2\text{Me})(\text{CH}_2\text{CH}_2\text{CO}_2\text{Me})^+$ (II). The free energy of

activation for this process is 18.7 kcal/mol and matches that based on the catalytic turnover frequency. This observation confirms I ($M = Rh$) as the resting state and the C:C coupling reaction as the turnover-limiting step. Treatment of II with Me acrylate results in rapid displacement of dimer to regenerate species I ($M = Rh$) and thereby closes the catalytic cycle.

- L5 ANSWER 17 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1992:235830 CAPLUS
DN 116:235830
TI Sequential displacement of coordinated ethene by hexafluorobenzene: crystal structures of η^2 - and η^4 -hexafluorobenzene complexes of iridium
AU Bell, Tanachat W.; Helliwell, Madeleine; Partridge, Martin G.; Perutz, Robin N.
CS Dep. Chem., Univ. York, York, YO1 5DD, UK
SO Organometallics (1992), 11(5), 1911-18
CODEN: ORGND7; ISSN: 0276-7333
DT Journal
LA English
AB The photochem. reaction of (η^5 -C₅R₅)Ir(C₂H₄)₂ ($R = H, Me$) with hexafluorobenzene effects sequential replacement of coordinated ethene by hexafluorobenzene, yielding (η^5 -C₅R₅)Ir(C₂H₄)(η^2 -C₆F₆) (I) followed by (η^5 -C₅R₅)Ir(η^4 -C₆F₆) (II). I is present in solution as two isomers which interconvert slowly compared with the NMR relaxation time, T₁. The dominant isomer of I exhibits coupling between ethene nuclei and ¹⁹F, suggestive of a C-H···F interaction. The minor isomer is postulated to be related to the major isomer by 180° rotation about the vector joining Ir to the midpoint of the coordinated C-C bond of C₆F₆. All the complexes exhibit three mutually coupled resonances in the ¹⁹F NMR spectrum, indicating that the C₆F₆ units are stereochem. rigid. The x-ray crystal structure of I and II ($R = H$) were determined
- L5 ANSWER 18 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1991:559400 CAPLUS
DN 115:159400
TI Metallacyclobutanes from kinetic nucleophilic addition to η^3 -allyl ethylene complexes of iridium. Regioselectivity dependence on nucleophile and allyl orientation
AU Wakefield, James B.; Stryker, Jeffrey M.
CS Dep. Chem., Indiana Univ., Bloomington, IN, 47405, USA
SO Journal of the American Chemical Society (1991), 113(18), 7057-9
CODEN: JACSAT; ISSN: 0002-7863
DT Journal
LA English
AB The addition of nucleophiles to both endo- and exo-isomers of the η^3 -allyl ethylene complex (C₅Me₅)Ir(η^2 -C₂H₄)(η^3 -C₃H₅) + OTf- has been investigated. Contrary to predictions based on the selectivity rules of Davies, Green, and Mingos (1978) kinetic nucleophiles such as hydride and organic enolates react regiospecifically at the η^3 -allyl central C, giving metallacyclobutane complexes. With the enolate of propiophenone, the two η^3 -allyl stereoisomers return metallacyclobutane products isomeric at the β -carbon, indicating that the nucleophile does not induce endo-exo isomerization prior to addition. Iodinolysis of the metallacyclobutanes at low temperature releases the organic as the substituted cyclopropane and returns the metal as [(C₅Me₅)IrI₂]₂, which can be converted back to the starting allyl ethylene complex in a single step. The reaction of weaker nucleophiles, such as potassium dimethylmalonate, does not lead to metallacyclobutane formation. Instead, these reactions reveal an unexpected regioselectivity dependence on the configuration of the allyl ligand: the exo-allyl complex returns exclusively an ethylene adduct, while the endo-allyl complex suffers addition to the terminal carbon of the allyl ligand. These results demonstrate a

considerably more complex reactivity profile than expected.

LS ANSWER 19 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1991:82070 CAPLUS
DN 114:82070
TI A dinuclear iridium aryldiazenide complex with a $\mu_2\text{-}\eta_2\text{-N,N'}$ bridge.
Synthesis of $[(C_5Me_5)_2Ir_2(CO)_2(\mu_2\text{-}\eta_2\text{-NNC}_6H_4OMe)][BF_4]$ from
 $[(C_5Me_5)Ir(C_2H_4)(N_2C_6H_4OMe)][BF_4]$
AU Einstein, Frederick W. B.; Yan, Xiaoqian; Sutton, Derek
CS Dep. Chem., Simon Fraser Univ., Burnaby, BC, V5A 1S6, Can.
SO Journal of the Chemical Society, Chemical Communications (1990),
(21), 1466-7
CODEN: JCCCAT; ISSN: 0022-4936
DT Journal
LA English
OS CASREACT 114:82070
GI



AB $[(C_5Me_5)Ir(C_2H_4)(p-N_2C_6H_4OMe)][BF_4]$ (I) and the nitrosyl analog $[(C_5Me_5)Ir(C_2H_4)(NO)][BF_4]$, have been synthesized from $(C_5Me_5)Ir(C_2H_4)_2$ and $[p-N_2C_6H_4OMe][BF_4]$ or $[NO][BF_4]$; I reacts with $(C_5Me_5)Ir(CO)_2$ to give the title dinuclear complex II (Cp^* = pentamethylcyclopentadienyl) in which the aryldiazenide ligand bridges in the four-membered dimetalladiaz-a-ring fashion.

LS ANSWER 20 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1990:515544 CAPLUS
DN 113:115544
TI Ethylene-assisted allylic carbon-hydrogen bond activation of substituted alkenes using dicationic iridium complexes. Synthesis, structure, and configurational isomerism of cationic iridium η^3 -allyl ethylene complexes
AU Wakefield, James B.; Stryker, Jeffrey M.
CS Dep. Chem., Indiana Univ., Bloomington, IN, 47405, USA
SO Organometallics (1990), 9(9), 2428-30
CODEN: ORGND7; ISSN: 0276-7333
DT Journal
LA English
OS CASREACT 113:115544
AB The use of ethylene as a sterically small, chemically inert, enabling ligand allows the dicationic iridium tris(solvate) complex $[Cp^*Ir(S)_3]^{2+}(OTf^-)_2$ (S = acetone, Cp^* = η^5 -C₅Me₅, OTf = triflate) to mediate allylic carbon-hydrogen bond activation of substituted olefins, giving monocationic η^3 -allyl complexes of the form $[Cp^*(C_2H_4)(\eta^3\text{-allyl})]^+$ OTf⁻, where the allyl is mono- or disubstituted, in high yield. In the absence of ethylene, the reaction fails for simple olefins larger than propene itself. This allylic activation selectively provides the thermodynamically less stable exo isomer of the allyl ligand. In the parent allyl ethylene complex, isomerization to the thermodyn. endo isomer is observed on treatment with triphenylphosphine; no substitution of the ethylene ligand is observed. Photolysis of the thermodyn. endo isomer returns the kinetic exo isomer. In contrast, the substituted crotyl ethylene

complex on treatment with triphenylphosphine leads to clean substitution of the thylene, providing $[Cp^*(Ph_3P)Ir(crotyl)]^+ OTf^-$. Isomerization of the kinetic exo isomer in the crotyl complex is obtained thermally in the absence of added ligand; quant. conversion is obtained by heating under ethylene to suppress decomposition by loss of the coordinated ethylene. Both the thermodyn. and endo allyl complex $[Cp^*Ir(C_2H_4)(\eta^3\text{-allyl})]^+ OTf^-$ and the kinetic exo crotyl complex $[Cp^*Ir(C_2H_4)(\eta^3\text{-crotyl})]^+ OTf^-$ have been characterized by x-ray crystallog. The reaction of 2-pentene with the dication leads to a mixture of isomeric terminal and internal $\eta^3\text{-allyl}$ complexes, with good selectivity for internal allylic activation.

L5 ANSWER 21 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1988:493287 CAPLUS
DN 109:93287
TI The formation and characterization of (η^2 -ethene)hydrido(η^5 -pentamethylcyclopentadienyl)(trisubstituted-silyl)rhodium complexes; intermediates in catalytic dehydrogenative silylation reactions
AU Ruiz, Jose; Bentz, Peter O.; Mann, Brian E.; Spencer, Catriona M.; Taylor, Brian F.; Maitlis, Peter M.
CS Dep. Chem., Univ. Sheffield, Sheffield, S3 7HF, UK
SO Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999) (1987), (11), 2709-13
CODEN: JCDTBI; ISSN: 0300-9246
DT Journal
LA English
OS CASREACT 109:93287
AB The complexes $[Cp^*Rh(H)(SiR_3)(C_2H_4)]$ (I; $Cp^* = C_5Me_5$; $C_5H_5 = \eta^5$ -cyclopentadienyl; R = Et, Me) were detected and characterized spectroscopically (including ^{103}Rh NMR spectra) as intermediates in the thermal and photochem. reaction, $C_2H_4 + [Cp^*Rh(H)_2(SiR_3)_2]$ (II) .dblharw. $[Cp^*Rh(C_2H_4)_2]$ (III) + R_3SiH . Complex I (R = OEt), which was isolated and fully characterized, and I (R = Ph), were obtained from reaction of R_3SiH and $[Cp^*Rh(C_2H_4)_2]$. Evidence for Ir analogs of I was observed, but reactions were more complex. I were reasonably thermally stable; since II and III are active catalysts for the reaction, $Et_3SiH + C_2H_4 \rightarrow CH_2:CHSiEt_3 + SiEt_4$, this implies significant activation is required to reorganize the ligands in I. The related reaction of R_3SiH (R = Me, Et, Ph, OEt) and $[Cp^*Rh(CO)_2]$ gave $[Cp^*Rh(CO)H(SiR_3)]$, which lost R_3SiH to give blue $[Cp^*Rh(CO)]_2$.

L5 ANSWER 22 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1988:168123 CAPLUS
DN 108:168123
TI Catalytic synthesis of olefins from paraffins in the presence of alkenes and catalyst manufacture
IN Walker, Howard Walter
PA Ethyl Corp., USA
SO Eur. Pat. Appl., 8 pp.
CODEN: EPXXDW
DT Patent
LA English
FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	EP 245061	A1	19871111	EP 1987-303970	19870501 <--
	EP 245061	B1	19891123		
	R: AT, BE, CH, DE, FR, GB, IT, LI, LU, NL, SE				
	US 4670621	A	19870602	US 1986-859696	19860505 <--
	US 4751344	A	19880614	US 1987-37231	19870416 <--
	AT 48128	T	19891215	AT 1987-303970	19870501 <--
PRAI	US 1986-859696	A	19860505		
	US 1987-37231	A	19870416		
	EP 1987-303970	A	19870501		

AB The photochem. or thermal dehydrogenation of saturated hydrocarbons uses catalytic transition metal complexes RMLnHm (R = Cp or arene which donates 6 electrons; M = transition metal of atomic number 43, 44, 45, 75, 76, or 77; L = alkene or cycloalkene, diene or cyclodiene, or triene or cyclotriene; n = 1, 2, or 3; M = 0 or 1) and free alkene hydrogen acceptors. Dehydrogenation of 59 mmol cyclooctane at 225° for 16 h under 300 psig in the presence of C₂H₄ and 52 μmol bis(ethylene)pentamethylcyclopentadienyl iridium gave 0.54% cyclooctene.

L5 ANSWER 23 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1987:617821 CAPLUS

DN 107:217821

TI The synthesis and characterization of dihydridobis(trialkylstannyl)(pentamethylcyclopentadienyl)rhodium(V) and -iridium(V) complexes and related reactions

AU Ruiz, Jose; Spencer, Catriona M.; Mann, Brian E.; Taylor, Brian F.; Maitlis, Peter M.

CS Dep. Chem., Univ. Sheffield, Sheffield, S3 7HF, UK

SO Journal of Organometallic Chemistry (1987), 325(1-2), 253-60
CODEN: JORCAI; ISSN: 0022-328X

DT Journal

LA English

OS CASREACT 107:217821

AB The complexes [C₅Me₅M(H)₂(SnR₃)₂] (I; M = Rh, Ir; R = Bu, Me) were prepd. by reaction of R₃SnH and [(C₅Me₅M)₂Cl₄] or [C₅Me₅M(C₂H₄)₂]. An intermediate in the last reaction was spectroscopically identified as [C₅Me₅M(H)(SnR₃)(C₂H₄)] (M = Ir, R = Me), but the Rh analog could not be detected. The hydrido carbonyl complexes, [C₅Me₅M(H)(SnR₃)(CO)] (same M, R) were readily obtained by reaction of R₃SnH with [C₅Me₅M(CO)₂]; they were more stable than their silyl analogs, but the Rh complexes slowly decomposed. I were very resistant to attack by nucleophiles, but I (M = Rh, R = Me) slowly reacted with PPh₃ to give [C₅Me₅Rh(PPh₃)(SnR₃)₂]; this behavior was in marked contrast to that shown by [C₅Me₅Rh(H)₂(SiR₃)₂]. The complex [C₅Me₅Rh(H)₂(SnMe₃)₂] was deprotonated by BuLi to give [C₅Me₅Rh(H)(SnMe₃)₂]⁻; this was reversed on addition of MeOH.

L5 ANSWER 24 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1987:536327 CAPLUS

DN 107:136327

TI Photochemical catalytic manufacture of alkenes from paraffins

IN Walker, Howard W.

PA Ethyl Corp., USA

SO U.S., 5 pp.

CODEN: USXXAM

DT Patent

LA English

FAN.CNT 2

	PATENT NO.	KIND	DATE	APPLICATION NO.	DATE
PI	US 4670621	A	19870602	US 1986-859696	19860505 <--
	US 4751344	A	19880614	US 1987-37231	19870416 <--
	CA 1277997	C	19901218	CA 1987-535816	19870428 <--
	EP 245061	A1	19871111	EP 1987-303970	19870501 <--
	EP 245061	B1	19891123		
	R: AT, BE, CH, DE, FR, GB, IT, LI, LU, NL, SE				
	JP 63022034	A	19880129	JP 1987-108736	19870501 <--
	JP 04040332	B	19920702		
	AT 48128	T	19891215	AT 1987-303970	19870501 <--
PRAI	US 1986-859696	A2	19860505		
	US 1987-37231	A	19870416		
	EP 1987-303970	A	19870501		

OS CASREACT 107:136327

AB The title process comprises transferring H from a saturated hydrocarbon to an alkene via a bis(alkene)cyclopentadienyl Ir mol. complex catalyst in the

presence of free alkene. The reaction may be performed photochem. under UV irradiation or thermolytically with the application of heat. By use of these catalysts it is now routinely possible to use alkenes in general as H acceptors, and while C₂H₄ is the preferred alkene, other alkenes may successfully be employed. Thus, 30 mg bis(ethylene)pentamethylcyclopentadienyl Ir and 2.83 g decane (pretreated with H₂SO₄, passed through silica gel and distilled under N) were charged into an autoclave, the apparatus pressured

to 150 psi with C₂H₄, shaken, and the pressure released. The autoclave was then pressurized with C₂H₄ to 150 psi and operated at 246°/340 psi for 19 h, and gas chromtog. anal. of the reaction mixture indicated the presence of C₂H₆ and 16% decenes having the isomer distribution 1-decene 9.58, 2-decene 29.17, 3-decene 30.25, and 4- and 5-decenes 31.22%.

L5 ANSWER 25 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1986:609169 CAPLUS

DN 105:209169

TI First example of cyclodimerization of a phosphaalkyne to a 1,3-diphosphacyclobutadiene. Syntheses of complexes of the type [M(η 5-C₅R₅) $\{\eta$ 4-Me₃CCP)₂] (R = H or Me; M = Co, Rh, or Ir): crystal and molecular structure of η 5-pentamethylcyclopentadienyl-2,4-di-tert-butyl-1,3-diphosphacyclobutadienecobalt(I), [Co(η 5-C₅Me₅) $\{\eta$ 4-(Me₃CCP)₂]

AU Hitchcock, Peter B.; Maah, Mohd Jamil; Nixon, John F.

CS Sch. Chem. Mol. Sci., Univ. Sussex, Brighton, BN1 9QJ, UK

SO Journal of the Chemical Society, Chemical Communications (1986), (10), 737-8

CODEN: JCCCAT; ISSN: 0022-4936

DT Journal

LA English

OS CASREACT 105:209169

GI For diagram(s), see printed CA Issue.

AB Reaction of the bisethylene complexes I (R = H, M = Co, Rh; R = Me, M = Co, Rh, Ir) with Me₃CC.tplbond.P in PhMe at room temperature gave 15-95% yield of the corresponding complexes II, containing the novel 2,4-di-tert-butyl-1,3-diphosphacyclobutadiene ring. The structures of II were determined by spectral methods and confirmed by x-ray crystallog. anal. of II (R = Me, M = Co).

L5 ANSWER 26 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1983:179617 CAPLUS

DN 98:179617

TI Approaches to ethyl(pentamethylcyclopentadienyl)rhodium or -iridium complexes

AU De Miguel, Amelio Vazquez; Maitlis, Peter M.

CS Dep. Chem., Univ. Sheffield, Sheffield, S3 7HF, UK

SO Journal of Organometallic Chemistry (1983), 244(2), C35-C37

CODEN: JORCAI; ISSN: 0022-328X

DT Journal

LA English

AB Reaction of [(C₅Me₅M)₂C₁₄] (M = Rh or Ir) with Al₂Et₆ gives [C₅Me₅M(C₂H₄)₂] and some [C₅Me₅MCl(η 3-CH₂CHCHMe)] but [C₅Me₅RhEt₂(PM₃)] is obtained from the reaction of [C₅Me₅RhCl₂(PM₃)] with Al₂Et₆.

L5 ANSWER 27 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN

AN 1979:137976 CAPLUS

DN 90:137976

TI Pentamethylcyclopentadienylrhodium and -iridium complexes. Part 18. The reactions of [M(C₅Me₅)(sol)₃][PF₆]₂ (M = Rh or Ir; sol = MeCN, Me₂CO, or MeOH) with mono-, di-, and triolefins

AU White, Colin; Thompson, Stephen J.; Maitlis, Peter M.

CS Dep. Chem., Univ. Sheffield, Sheffield, UK

SO Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999) (1978), (10), 1305-11

CODEN: JCDTBI; ISSN: 0300-9246
DT Journal
LA English
AB [ML(MeCN)3][PF6]2 (M = Rh, Ir; L = pentamethylcyclopentadienyl) or [MLCl2]2 reacted with bicyclo[2.2.1]heptadiene, 1,5-cyclooctadiene, propene, dicyclopentadiene, and cycloheptatriene to give 9 η-olefin complexes, e.g. [MLL1][PF6]2 (L1 = η-cyclooctadienyl, 1,2,3,4,5-η-6-acetonyl cycloheptadienyl) which were characterized by anal. and NMR data. The olefins were deprotonated by [ML(Me2CO)3][PF6]2, except for cycloheptadiene, which underwent nucleophilic attack by the solvent with [ML(XH)n][PF6]2 (XH = Me2CO, M = Rh, Ir; XH = MeOH, M = Rh) to give [MLL2][PF6] (L2 = 6-exo-acetonyl-, 6-exo-methoxy-1,2,3,4,5-η-cycloheptadienyl). The 13C and 1H NMR spectra are reported and discussed.

L5 ANSWER 28 OF 28 CAPLUS COPYRIGHT 2007 ACS on STN
AN 1971:3721 CAPLUS
DN 74:3721
TI Pentamethylcyclopentadienyl-rhodium and -iridium halides. II. Reactions with mono-, di-, and triolefins
AU Maitlis, Peter M.; Moseley, K.; Kang, Jung W.
CS Dep. Chem., McMaster Univ., Hamilton, ON, Can.
SO Journal of the Chemical Society [Section] A: Inorganic, Physical, Theoretical (1970), (17), 2875-83
CODEN: JCSIAP; ISSN: 0022-4944
DT Journal
LA English
AB Dimeric dichloropentamethylcyclopenta-dienylrhodium and -iridium complexes, [M(C5Me5)Cl2]2 (M = Ir, Rh), reacted in ethanol in the presence of Na2CO3 with butadiene, cycloheptatriene, and 6,6-diphenylfulvene, giving pentamethylcyclopentadienylrhodium(III) or -iridium(III) complexes of π-1-methylallyl, π-cyclohepta-2,4-dienyl, and (1,1-diphenylmethyl)cyclopentadienyl. Under similar conditions with [Rh(C5Me5)Cl2]2, norbornadiene and dicyclopentadiene gave pentamethylcyclopentadienylrhodium(I) diene complexes: ethylene gave bis(ethylene)rhodium(I) and -iridium(I) complexes. A hydrido-intermediate is implied in these reactions and both the hydrido- and deuteriochloro(triphenylphosphine)pentamethylcyclopentadienyliridium complexes were isolated and characterized. With cyclopentadiene, [Rh(C5Me5)Cl2]2 gave the cation and (cyclopentadienyl)-endo-H-pentamethylcyclopentadienylrhodium(I). (Cyclopentadienyl)-exo-H-pentamethylcyclopentadienylrhodium(I) was obtained by reduction of [Rh(C5Me5)(C5H5)]+ with NaBH4 and was much more reactive than the endo-H-isomer. With halogenating agents, [RH(C5Me5)(C5H5)]+ was the product, whereas the endo-H-isomer underwent cleavage to [Rh(C5Me5)X2]2 and [Rh(C5H5)X2]2. [Ir(C5Me5)Cl2]2 reacted with cyclopentadiene to give only the [Ir(C5Me5)(C5H5)]+ cation, which on reduction gave exo-H-Ir(C5Me5H)(C5H5) and Ir(C5Me5)(C5H6).